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# Spatial and Seasonal Variability of Dissolved Methylmercury in Two Stream Basins in the Eastern United States

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S *Supporting Information*

**ABSTRACT:** We assessed methylmercury (MeHg) concentrations across multiple ecological scales in the Edisto (South Carolina) and Upper Hudson (New York) River basins. Out-of-channel wetland/floodplain environments were primary sources of filtered MeHg (F-MeHg) to the stream habitat in both systems. Shallow, open-water areas in both basins exhibited low F-MeHg concentrations and decreasing F-MeHg mass flux. Downstream increases in out-of-channel wetlands/floodplains and the absence of impoundments result in high MeHg throughout the Edisto. Despite substantial wetlands coverage and elevated F-MeHg concentrations at the headwater margins, numerous impoundments on primary stream channels favor spatial variability and lower F-MeHg concentrations in the Upper Hudson. The results indicated that, even in geographically, climatically, and ecologically diverse streams, production in wetland/floodplain areas, hydrologic transport to the stream aquatic environment, and conservative/nonconservative attenuation processes in open water areas are fundamental controls on dissolved MeHg concentrations and, by extension, MeHg availability for potential biotic uptake.


## INTRODUCTION

Controls on production, transport, and bioaccumulation of methylmercury (MeHg) are less understood in streams than lakes, because spatial/temporal separation of potential MeHg sources and biotic habitats in extended stream reaches obscures important ecological linkages.[1] Wetlands are areas of Hg methylation and elevated MeHg concentrations.[2−5] Positive correlations between fish Hg burdens, dissolved MeHg concentrations, and basin wetland densities[2−6] indicate that wetlands may be the proximal source of MeHg in stream biota. Lack of correlation between MeHg concentrations in surface water (or indigenous fish) and in underlying bed sediment in a multibasin investigation[6,7] emphasized the importance of upstream MeHg sources.

We assessed MeHg at large basin ($\geq$200 km$^2$), headwater basin ($\leq$80 km$^2$), and stream reach scales in two basins (Edisto River, South Carolina; Upper Hudson River, New York) with elevated fish Hg burdens. Spatial/seasonal patterns in surface water dissolved MeHg concentrations and mass fluxes were assessed along with sediment MeHg concentrations and production potentials in the headwater basins to identify MeHg sources and important controls on stream MeHg concentrations throughout the Edisto and Upper Hudson Rivers.

## MATERIAL AND METHODS

**Study Basins.** The Edisto River basin (Figure 1) is in the Coastal Plain of South Carolina, free-flowing (no dams), and characterized by low-stream gradients and extensive riparian wetlands.[8,9] Hg burdens in largemouth bass (*Micropterus salmoides*) in the Edisto are among the highest for top predator fish in the United States.[10] Potential out-of-channel MeHg source areas at the McTier Creek headwater basin included macrophyte-dominated perennial wetlands and transiently flooded riparian pools. Shallow beaver ponding existed in Gully Creek (GC), primarily between GC1 and GC2 sampling locations. Gravatt Pond (within MC3; not shown) was included to assess the potential impact of small man-made impoundments.

The Upper Hudson River basin is located in the Adirondack province of the Appalachian Highlands of New York. The Fishing Brook headwater basin included Fishing Brook, its primary tributary (Six Mile Brook), several smaller tributaries

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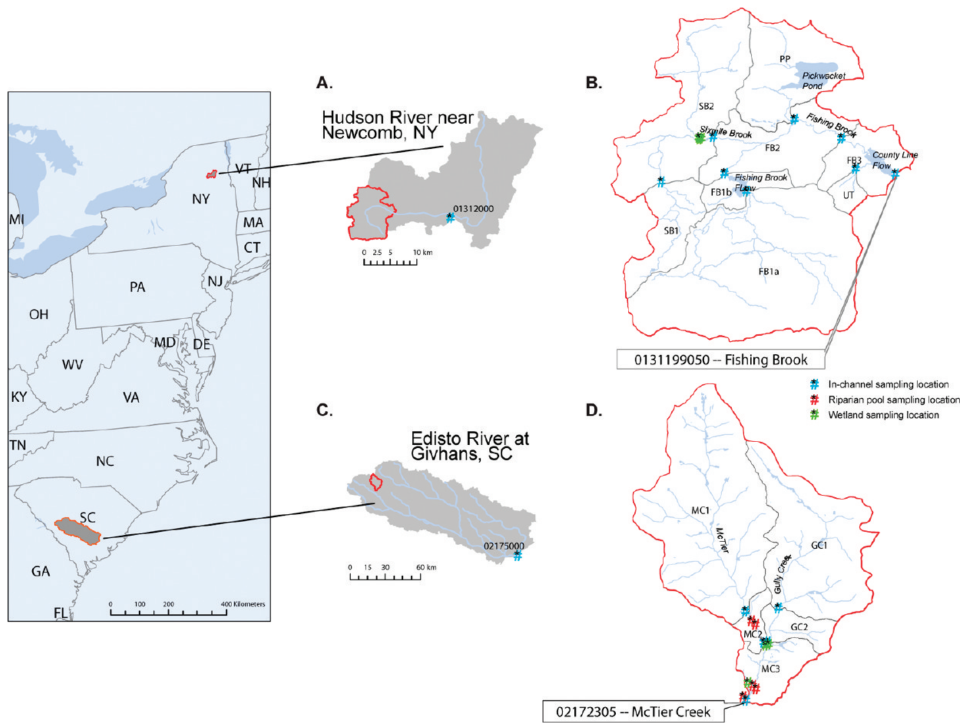


**Figure 1.** (A.) Upper Hudson River basin with gage 01312000 (▲ (blue), Hudson River near Newcomb, NY) and Fishing Brook headwater basin (red outline). (B.) Fishing Brook study basin showing reach boundaries, along with in-stream (▲ (blue)) and wetland seep (▲ (green)) sampling locations. (C.) Edisto River basin with gage 02175000 (▲ (blue), Edisto River near Givhans, SC) and McTier Creek headwater basin (red outline). (D.) McTier Creek study basin showing reach boundaries, along with in-stream (▲ (blue)), wetland (▲ (green)), and riparian pool (▲ (red)) sampling locations.

**Table 1. Selected Landscape Characteristics[8] for the Entire Upstream Drainage Area and the Drainage Area Unique to Each Reach in the McTier Creek and Fishing Brook Areas**

| | | | upstream drainage | | | | reach drainage | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| study area | description | ID | area (km$^2$) | slope (%) | wetland (%) | open water (%) | area (km$^2$) | slope (%) | wetland (%) | open water (%) |
| McTier Creek | Gully Creek | GC1 | 25.9 | 6.3 | 6.4 | 1.3 | 25.9 | 6.3 | 6.4 | 1.3 |
| | Gully Creek | GC2 | 29.9 | 6.2 | 7.0 | 1.2 | 4.0 | 5.4 | 11.0 | 0.1 |
| | McTier Creek | MC1 | 40.5 | 6.2 | 7.3 | 1.0 | 40.5 | 6.2 | 7.3 | 1.0 |
| | McTier Creek | MC2 | 42.9 | 6.2 | 8.0 | 0.9 | 2.4 | 4.8 | 20.2 | 0 |
| | McTier Creek | MC3 | 79.4 | 6.1 | 8.2 | 1.0 | 6.6 | 4.9 | 14.4 | 1.6 |
| Fishing Brook | Pickwackett Pond | PP | 8.4 | 16.4 | 5.2 | 11.4 | 8.4 | 16.4 | 5.2 | 11.4 |
| | Six Mile Brook | SB1 | 4.6 | 10.4 | 5.7 | 1.1 | 4.6 | 10.4 | 5.7 | 1.1 |
| | Six Mile Brook | SB2 | 17.7 | 11.9 | 13.9 | 1.0 | 13.2 | 12.5 | 16.7 | 1.0 |
| | Unnamed Tributary | UT | 1.0 | 29.0 | 0 | 0 | 1.0 | 29.0 | 0 | 0 |
| | Fishing Brook | FB1a | 25.0 | 19.6 | 5.5 | 0.1 | 25.0 | 19.6 | 5.5 | 0.1 |
| | Fishing Brook | FB1b | 27.1 | 18.8 | 6.4 | 1.1 | 2.1 | 8.9 | 16.3 | 12.5 |
| | Fishing Brook | FB2 | 60.6 | 15.5 | 9.5 | 2.4 | 33.5 | 12.9 | 15.4 | 0 |
| | Fishing Brook | FB3 | 65.6 | 15.7 | 9.3 | 3.0 | 5.0 | 18.3 | 6.7 | 11.3 |

(including Unnamed Tributary) and three named, shallow (mean depth less than 2 m) open water bodies (Fishing Brook Flow, Pickwacket Pond, and County Line Flow).

**Surface-Water MeHg Flux Sampling Network.** Reaches with distinct hydrologic/ecologic characteristics were established throughout each headwater basin (Table 1; Figure 1). Herein, reach includes the drainage area associated with the designated stream extent. Filtered MeHg (F-MeHg) concentrations were used to assess spatial/seasonal variations in MeHg availability in the stream habitat. Instantaneous F-MeHg mass flux (mg/d; concentration times local discharge measured by acoustic Doppler) was used to evaluate relative contributions from individual reaches and to distinguish conservative/nonconservative attenuation. F-MeHg yields ($\mu$g/ha/d; flux divided by drainage area) for individual stream reaches were calculated as the difference in yields between downstream and upstream reach margins. Yields at basin margins were assumed to be zero.

Sampling events covered a range of seasons and hydrologic conditions. Sampling at McTier was completed within 6−8 h. No systematic change in discharge (approximate steady state)


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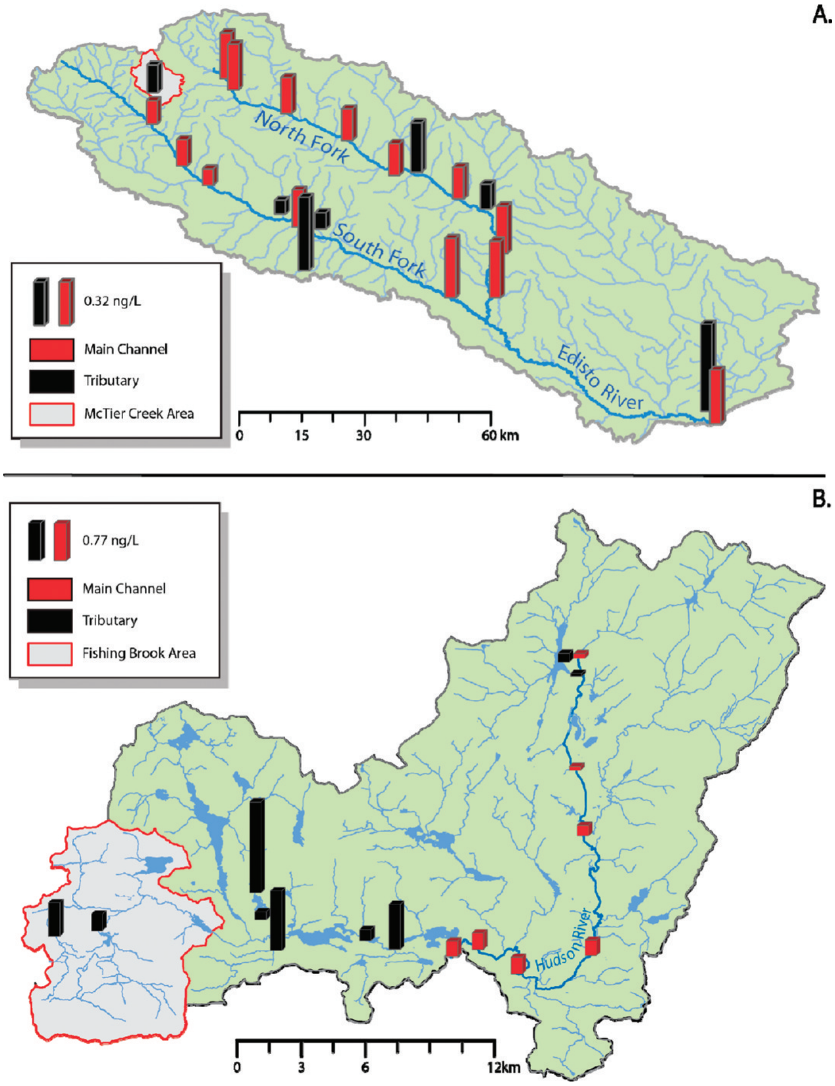


**Figure 2.** Unfiltered methylmercury (U-MeHg) concentrations (ng/L) at tributary and main-channel locations throughout the (A) Edisto and (B) Upper Hudson basins in 2006.

was observed at the gage during sampling. Fishing Brook sampling was completed within 2−3 days, during slowly receding streamflow conditions. Streamflow variation (standard deviation of mean streamflow) generally was less than 25%.

Out-of-channel locations were deemed probable sources of F-MeHg if concentrations exceeded those in the adjacent stream. F-MeHg concentrations were assessed in three perennial wetland and six riparian pool locations at McTier. Three groundwater seeps within a perennial wetland (SB2) were monitored at Fishing Brook.

**MeHg Sample Collection and Analysis.** USGS ultratrace-level sampling, processing, and analyses were as described.[2] The MeHg reporting limit was 0.04 ng/L. Surface sediment (0−2 cm) was collected during 2008 from 4 in-channel and 3−4 out-of-channel locations. Sediment MeHg concentrations[11] and MeHg production potential (MPP) rates[12] were determined as described.[11,12]

**Statistical Analyses.** Significant differences in F-MeHg concentrations/yields were identified by nonparametric one-way analysis of variance (Kruskal−Wallis; $p \leq 0.05$) and multiple comparison analysis (Tukey's Honestly Significantly Different (HSD) test; $p \leq 0.05$).[13,14] Paired comparisons of upstream/downstream locations by event employed Prentice-Wilcoxon signed rank test ($p \leq 0.05$).

## RESULTS AND DISCUSSION

**U-MeHg Spatial Patterns in Large Basins.** Unfiltered MeHg (U-MeHg) samples were collected to assess large-basin spatial variation. Increasing U-MeHg concentrations with increasing distance downstream (Simple Linear Regression; $r^2$ = 0.40; $p$ = 0.003) indicated a continuous supply of MeHg to the stream throughout the Edisto basin. U-MeHg in Edisto main channel samples ranged 0.12−0.43 ng/L (median = 0.27; $n$ = 14). U-MeHg in Edisto tributaries ranged 0.10−0.63 ng/L (median = 0.20; $n$ = 7), with 0.20 ng/L detected at the McTier Creek location (Figure 2). The percentage of F-MeHg in U-MeHg water was greater than 80%, based on 2005−2009 data from gage 02175000 and from McTier Creek. This pattern is consistent with the increase in wetlands coverage from 5 to 10% in headwater basins like McTier Creek (Table 1) to greater than 20% downstream in the Edisto basin[8] and with the recognized

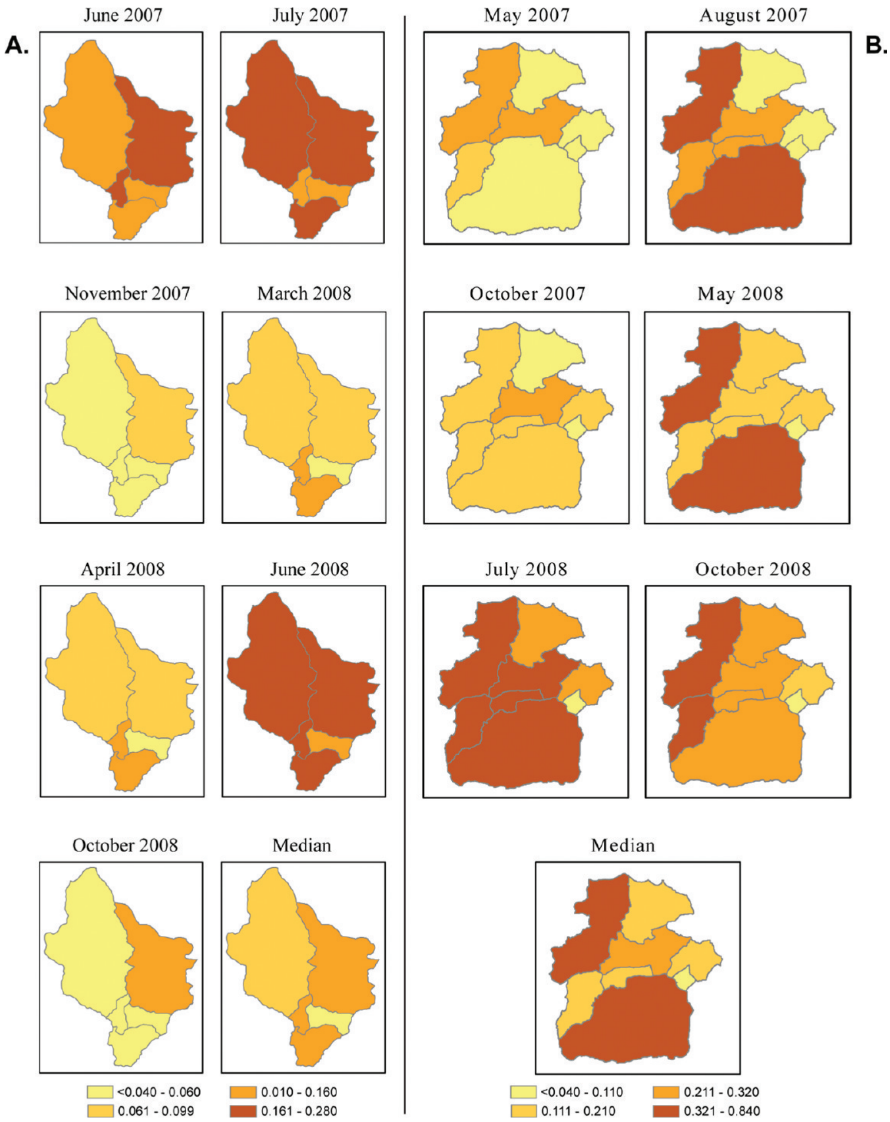


**Figure 3.** Filtered methylmercury (F-MeHg) concentrations (ng/L) at in-stream locations in the McTier Creek and Fishing Brook basins in 2007–2008. Categories are quartiles of all data for each basin.

role of wetlands as source areas for MeHg.[2−5] Thus, identifying environmental characteristics that favor consistent MeHg supply to the stream habitat is fundamental to understanding MeHg bioaccumulation in the Coastal Plain, an area with extensive fish Hg advisories and that extends from Texas to New Jersey.[9]

Elevated MeHg concentrations in tributary locations compared with the main channel indicated that significant sources of MeHg exist in headwater basins in the Upper Hudson basin but that environmental factors attenuate concentrations as water moves downstream. Main-channel U-MeHg in the Upper Hudson ranged 0.07–0.29 ng/L (median = 0.26; $n = 7$), while concentrations as high as 1.5 ng/L were observed in tributaries. U-MeHg in Fishing Brook ranged 0.19–0.57 ng/L (median = 0.25; $n = 4$). The percentage of F-MeHg in U-MeHg water was greater than 85%, based on 2005–2009 data from 01312000. Identifying headwater MeHg sources areas as well as the locations and mechanisms of downstream attenuation are fundamental to understanding the dynamics of Hg across multiple ecological scales in the Adirondacks.

**In-Stream F-MeHg Concentrations in Headwater Basins: Spatial Patterns.** *McTier Creek.* Little consistent spatial variation in F-MeHg concentrations was observed across sampling events (Figure 3), in agreement with the comparable U-MeHg concentrations throughout the Edisto basin and generally low stream gradients and uniform wetlands coverage at McTier. Combining all 7 synoptic sampling events, no statistical difference (Kruskal–Wallis; $p = 0.51$) in median F-MeHg concentrations was observed among reaches (Figure 4A). Lack of spatial variation suggests that MeHg source areas and good hydrologic connectivity to the stream are common at McTier and throughout the Edisto.

Consistently low F-MeHg concentrations at the downstream Gully Creek location (GC2) and Gravatt Pond suggested that the availability of MeHg for potential biotic uptake is low in open water areas. FMeHg concentrations at GC2 were significantly lower (Paired Prentice-Wilcoxon Test; $p = 0.008$) than at the upstream location (GC1) throughout the study, decreasing by 25–67%. This pattern suggests either dilution or a systematic F-MeHg loss (e.g., photodemethylation, sedimentation) in GC2.

*Fishing Brook.* Substantial spatial variation in F-MeHg concentrations was observed (Figure 3), in marked contrast to the McTier Creek area but consistent with the spatial variability in

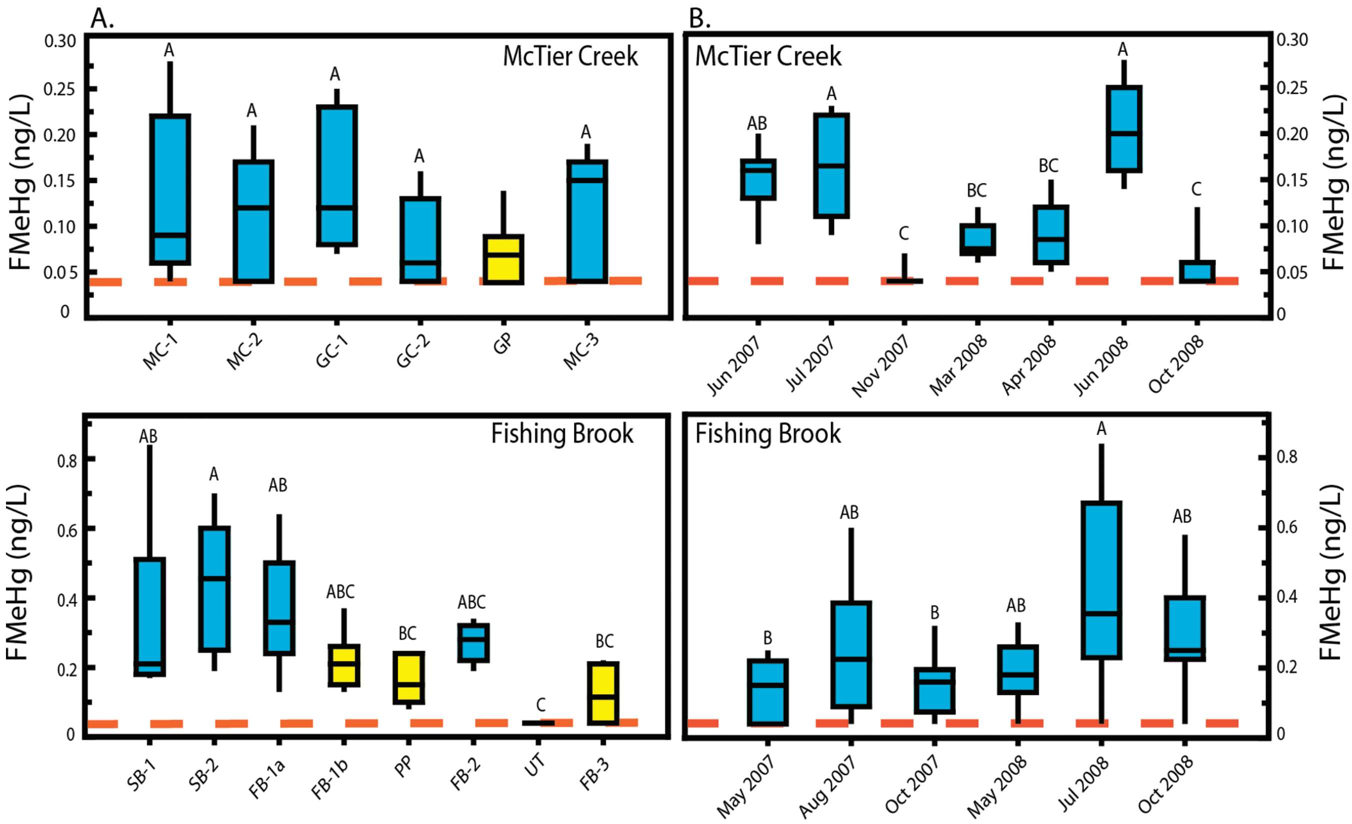


**Figure 4.** Filtered methylmercury (F-MeHg) concentrations (ng/L) at McTier Creek and Fishing Brook during 2007−2008 (A) by reach and (B) by event. Yellow indicates reaches with shallow open-water. Box indicates 25−75% quartile range. Centerline indicates median. Whiskers indicate data range. Same letter indicates differences were not statistically significant ($p > 0.05$; Kruskal−Wallis and Tukey's HSD).

MeHg concentrations in the Upper Hudson basin and with the range of stream gradients and wetland coverages in the Fishing Brook and Six Mile Brook basins (Table 1). Combining all 6 synoptic sampling events, significant differences (Kruskal−Wallis; $p = 0.003$) were apparent among reaches (Figure 4A).

F-MeHg concentrations were consistently low in reaches dominated by shallow, open-water. Median concentrations downstream of Fishing Brook Flow (FB1b), Pickwackett Pond (PP), and County Line Flow (FB3) were the lowest observed in the Fishing Brook study area, excluding Unnamed Tributary (which had no significant wetlands coverage). The median F-MeHg concentration downstream of Fishing Brook Flow (FB1b) was about 30% lower than that observed in Fishing Brook at the FB1a sampling location, immediately upstream. The median F-MeHg concentration at County Line Flow decreased (Paired Prentice-Wilcoxon Test; $p = 0.027$) by more than 50% between the upstream location (FB2) and the outflow at FB3. This pattern suggests either dilution or a systematic F-MeHg loss (e.g., photodemethylation, sedimentation) in impounded areas at Fishing Brook basin.

Reach wetland coverage expressed as a percentage of the total area or of the saturated (wetland plus open-water) area was a significant predictor of reach F-MeHg concentration, accounting for 46% (Simple Linear Regression; $r^2 = 0.46$; $p = 0.05$) and 75% (Simple Linear Regression; $r^2 = 0.75$; $p = 0.005$) of the variation in median F-MeHg, respectively. Lack of F-MeHg in unnamed tributary (no wetlands) is consistent with wetlands as a MeHg source at Fishing Brook.

**In-Stream F-MeHg Concentrations in Headwater Basins: Seasonal Patterns.** Seasonal variation in F-MeHg concentrations was significant at McTier Creek (Kruskal−Wallis; $p < 0.0001$) (Figure 4B). Maximum F-MeHg concentrations were observed in the summer. Median F-MeHg concentrations fell below the reporting limit in the fall. Water temperatures in McTier Creek ranged 18−35 °C (median =26 °C) during June/July and 8−23 °C (median =15 °C) during October/November.

Significant (Kruskal−Wallis; $p = 0.04$) seasonal variation in F-MeHg concentrations also was observed at Fishing Brook. Despite lower water temperatures in October (Fishing Brook range 5−16 °C, median = 10 °C), F-MeHg concentrations were substantially higher at Fishing Brook than at McTier Creek. The fact that comparable F-MeHg concentrations were observed at Fishing Brook during both May events, conducted immediately after snowmelt (water temperature range 7−16 °C, median =10 °C), indicates that the supply of F-MeHg to the aquatic habitat at Fishing Brook may remain important during the winter.

**F-MeHg Yields in Headwater Basins: Spatial Patterns.** Significant (Krukal-Wallis; $p = 0.019$) spatial variation in reach F-MeHg yields was observed at McTier Creek (Figure 5). F-MeHg yields were positive for all reaches except MC2 and GC2. Median F-MeHg yields in the MC3 reach were at least 3 times higher than in any other reach. The MC3 reach encompassed 8% of the basin area but, on average, contributed 21% of the total mass of F-MeHg (Paired Prentice-Wilcoxon Test; $p = 0.035$) and 13% of the total discharge (Paired Prentice-Wilcoxon Test; $p = 0.004$) observed at the downstream boundary of the study area.

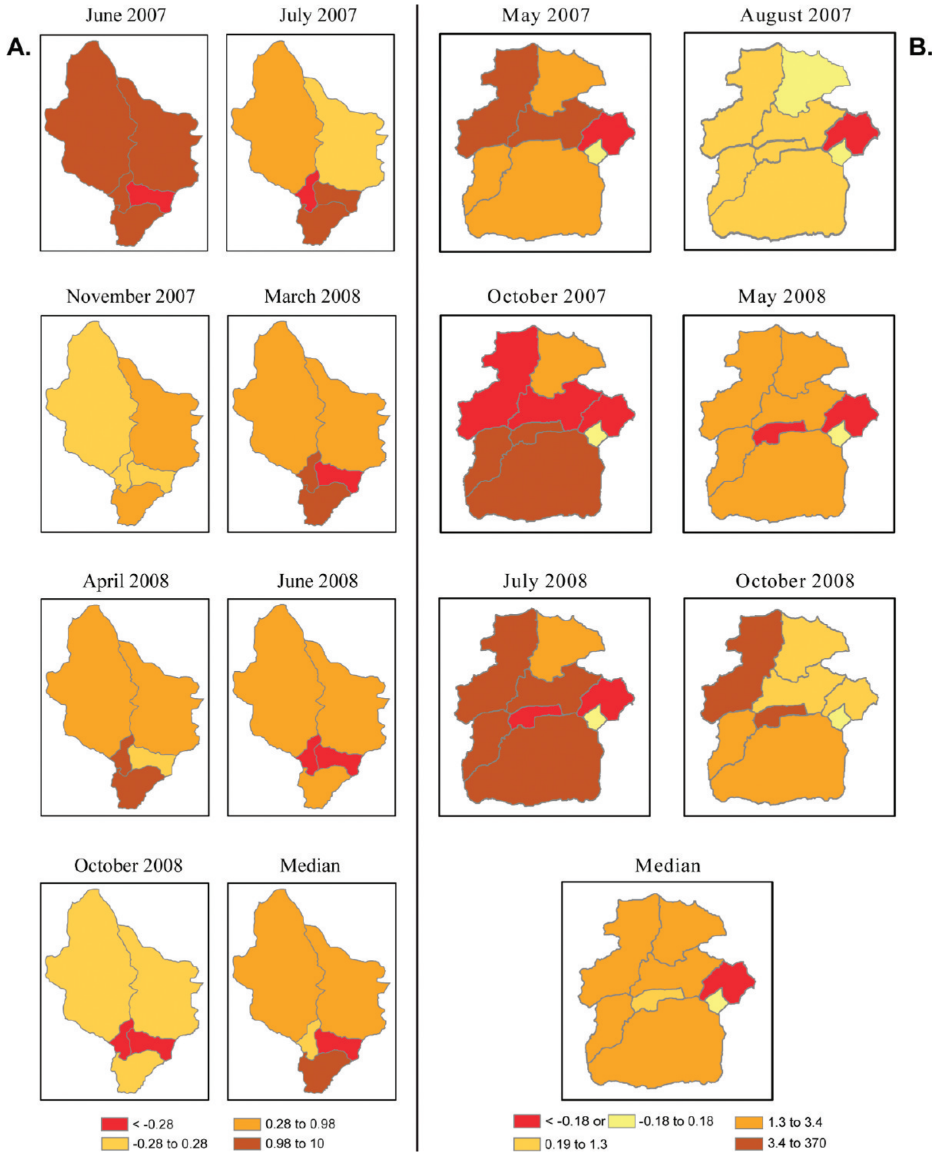


**Figure 5.** Reach filtered methylmercury (F-MeHg)($\mu$g/ha/d) yields at McTier Creek and Fishing Brook basins in 2007−2008. Fishing Brook October 2007 data were omitted due to changing flow conditions. Categories are quartiles of data for each basin. For McTier Creek, red indicates corresponding (0−25% quartile) reach yields were negative. Fishing Brook 0−25% quartile is divided into separate colors with red indicating negative reach yields.

No consistent change in F-MeHg mass was observed in MC2, indicating MC2 was not a primary F-MeHg source to the stream during the study. In contrast to all other McTier reaches, the median yield for GC2 was negative. Mass losses (Paired Prentice-Wilcoxon Test; $p = 0.023$) indicate that decreasing concentrations in the GC2 reach were not due to dilution. F-MeHg mass loss in the beaver impounded GC2 reach may be due to photodemethylation/evasion or sedimentation in shallow open-water.[15−18]

Significant (Kruskal−Wallis; $p = 0.008$) spatial variation in reach F-MeHg yields was also observed at Fishing Brook. In contrast to the spatial variation in concentrations, comparable positive F-MeHg yields were observed everywhere except FB3. This lack of variability in F-MeHg yields upstream of FB3 indicates a general similarity in the supply of F-MeHg to the stream, while significant variation in F-MeHg concentrations suggests differences in the potential for Hg bioaccumulation.[6]

Although small decreases in F-MeHg yields in two sampling events suggest a mass loss mechanism in Fishing Brook Flow, the positive median yield in FB1b indicates that the general decline in F-MeHg concentrations observed in this reach was at least partially attributable to dilution. In contrast, F-MeHg flux decreased (Paired Prentice-Wilcoxon Test; $p = 0.02$) in FB3, indicating systematic loss of F-MeHg mass in County Line Flow, consistent with enhanced Hg photodemethylation/evasion or sedimentation in open water.[15−18]

**In-Channel and Out-of-Channel Comparisons in Headwater Basins.** F-MeHg concentrations in wetlands and riparian pools were equal to or greater than in the adjacent McTier Creek channel (Figure 6). Generally higher F-MeHg concentrations and water levels in out-of-channel areas combined with increasing downstream discharge indicate that riparian margins are the primary source of F-MeHg in McTier Creek. Substantially higher sediment MeHg concentrations and MPP rates observed in out-of-channel locations compared with in-channel locations support this conclusion.


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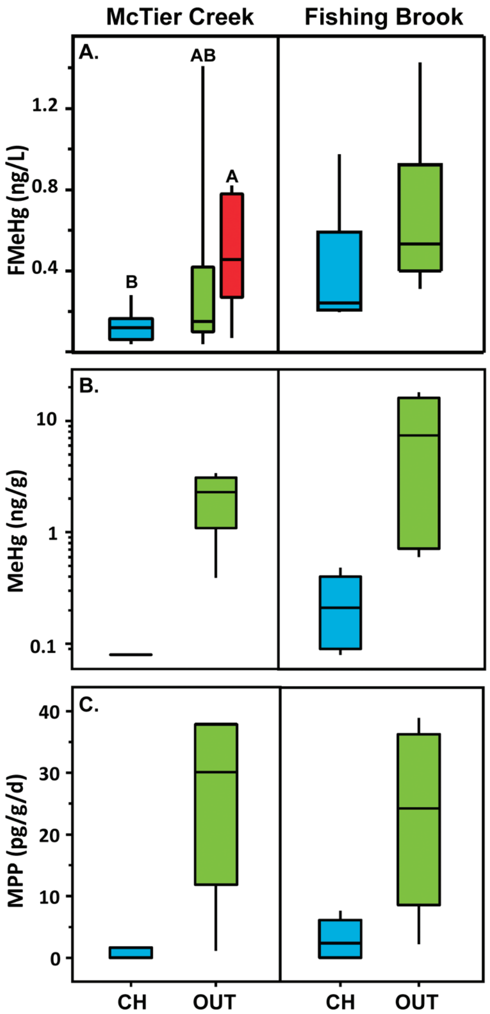


**Figure 6.** (A) Surface-water filtered methylmercury (F-MeHg) concentrations during 2007−2008, (B) surface sediment (0−2 cm) methylmercury (MeHg) concentrations in June 2007, and (C) methylmercury production potential (MPP) rates during June 2007 for in-channel (CH; blue) and out-of-channel (OUT; green) samples from McTier Creek and Fishing Brook. Box indicates 25−75% quartile range. Centerline indicates median. Whiskers indicate data range. Wetland (green) and riparian pool (red) data are separate for McTier Creek. Fishing Brook surface water data are for Sixmile Brook. Same letter indicates differences were not statistically significant ($p > 0.05$; Kruskal−Wallis and Tukey's HSD).

Higher F-MeHg concentrations and water levels at the Six Mile Brook groundwater seep locations than in the adjacent stream combined with increasing downstream discharge indicate that riparian margins also are primary F-MeHg source areas at Fishing Brook. Substantially higher sediment MeHg concentrations and MPP rates observed in out-of-channel locations compared with in-channel locations support this conclusion, as does the strong correlation between F-MeHg concentrations and wetlands coverage.

**Implications for Large Basin F-MeHg Concentration Patterns.** Out-of-channel wetland/floodplain environments appear to be primary sources for F-MeHg in the stream habitats at McTier Creek and Fishing Brook. Likewise, shallow, open-water locations, in both ecosystems, were areas of F-MeHg mass loss, comparatively low observed F-MeHg concentrations, and, by extension, diminished MeHg availability for potential biotic uptake.[6]

These results indicate that MeHg production in wetland/floodplain areas, hydrologic transport to the stream aquatic environment, and attenuation in open water areas prior to uptake are fundamental controls on F-MeHg concentrations in lotic habitats in diverse geographic, climatic, and ecologic settings. Although mechanisms were not explicitly studied, plausible explanations for F-MeHg loss in shallow open-water at McTier Creek and Fishing Brook include photodegradation with evasion and/or sedimentation.[15−18] It is noteworthy that the long-term impoundments at Fishing Brook appear to be relatively stable, biogeochemically. New and/or hydrodynamically unstable impoundments have been shown to exacerbate MeHg producstion.[19−21]

Consistently high wetlands coverage,[8] high hydrologic connectivity,[9] and groundwater-driven flooding in Coastal Plain rivers like the Edisto[9] favor widespread production and transport of F-MeHg to the stream habitat. The low F-MeHg concentrations observed in reach GC2 and in the Gravatt Pond tributary indicate that shallow open-water bodies attenuate F-MeHg concentrations in this ecologic setting. However, the Edisto River is the longest free-flowing (no dams) "black-water" stream in the eastern US. Downstream increases in out-of-channel wetlands/floodplains, combined with a lack of impoundments result in high MeHg in the Edisto basin. In contrast, despite substantial wetlands coverage and elevated F-MeHg concentrations at the headwater margins, numerous impoundments on primary stream channels favor spatial variability and lower F-MeHg concentrations in the Upper Hudson River.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Sampling/analysis details, regressions of MeHg against stream distance, and wetlands area. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION


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